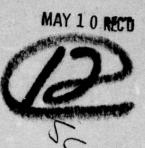


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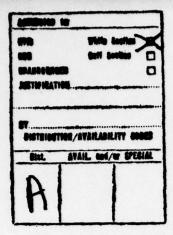




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SYNTHESES OF PHOSPHATRIAZINES FOR POTENTIAL HIGH TEMPERATURE FLUIDS APPLICATIONS

Contract No. F44620-76-C-0065

Final Report, SN-8296-F

30 April 1979

Ultrasystems, Inc. 2400 Michelson Drive Irvine, California 92715

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20. A series of six and eight membered heterocycles containing phosphorus, carbon and nitrogen atoms in the ring were synthesized. The specific classes of compounds prepared were monophospha-s-triazines, diphospha-s-triazines, diphospha-s-triazines in the presence of perfluoroalkylether side chains on the carbon ring atoms rendered the resulting compounds liquids at room temperature; substitution by perfluoroalkyl groups led to solids. Both the mono and diphospha-s-triazines were found to be effective anti-corrosion additives for perfluoroalkylether type fluids.

The monophospha-s-triazines were prepared in yields of 50-75% from the respective imidoylamidines and trichlorophosphoranes. The physical properties of the corresponding phenyl and pentafluorophenyl monophospha-s-triazines did not differ significantly.

The diphospha-s-triazines were synthesized in yields of 30-65% by interaction of imido-tetraphenyl-diphosphinic acid trichloride and the respective amidines.

The above synthetic approaches were successfully extended to the formation of dumbbell compounds.

Thermal and thermal oxidative stability evaluations were performed on mono and diphospha-s-triazines at 235 and 316°C using sealed Pyrex ampoules. All compounds wherein phenyl groups were present on the phosphorus exhibited good thermal stability up to 316°C; the analogous pentafluorophenyl substituted materials were degraded extensively at these temperatures. The oxidative stability of both the mono and diphospha-s-triazines was excellent at 235°C, but at 316°C some degradation was observed. This was more pronounced in compounds containing the perfluoroalkyl moiety on carbon than in the perfluoroalkylether substituted members of the series.

The symmetrical diphosphatetraazacyclooctatetraenes were obtained from the interaction of perfluoroalkyletheramidines and trichlorophosphoranes. Using this procedure, a mixture of products was afforded. The unsymmetrical isomers were prepared in excellent yields, >80%, from perfluoroalkyletherimidoylamidines and imido-tetraphenyl-diphosphinic acid trichloride.

FOREWORD

This Final Report describes the work performed by the Chemicals and Materials Research Department, Ultrasystems, Inc. under Contract F44620-76-C-0065, "Syntheses of Phosphatriazines for Potential High Temperature Fluids Applications." The investigations were carried out during the period from 1 March 1976 to 28 February 1979 by J. Kaufman, J. H. Nakahara, T. I. Ito, R. H. Kratzer, and K. L. Paciorek, Project Manager. This contract was administered by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, with Dr. Anthony J. Matuszko as Technical Program Manager.

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ABSTRACT

A series of six and eight membered heterocycles containing phosphorus, carbon and nitrogen atoms in the ring were synthesized. The specific classes of compounds prepared were monophospha-s-triazines, diphospha-s-triazines, and diphosphatetraazacyclooctatetraenes. The presence of perfluoroalkylether groups on the carbon ring atoms rendered the resulting compounds liquids at room temperature; substitution by perfluoroalkyl groups invariably led to solids. Both the mono- and diphospha-s-triazines were found to be effective anti-corrosion additives for perfluoroalkylether type fluids.

The monophospha-s-triazines, namely 1-diphenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine, 1-diphenylphospha-3,5-bis[C_3F_7 -[OCF(CF_3)CF $_2$] $_x$ OCF(CF_3)]-2,4,6-triazine (x = 1 and 2), and the penta-fluorophenyl-substituted analogues were prepared, in yields of 50-75%, from the respective imidoylamidines and trichlorophosphoranes. The physical properties of the corresponding phenyl and pentafluorophenyl monophospha-s-triazines did not differ significantly. On electron impact, the ion $R_2PN_2C^+$ (R = C_6H_5 or C_6F_5) constituted the base peak.

The diphospha-s-triazines, namely 1,3-bis(diphenylphospha)-5-perfluoro-n-heptyl-2,4,6-triazine and 1,3-bis(diphenylphospha)-5-perfluoro-alkylether-2,4,6-triazines, $[(C_6H_5)_2PN]_2[C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)CN]$ (x = 1 and 2) were synthesized in yields of 30-65% by interaction of imidotetraphenyl-diphosphinic acid trichloride and the respective amidines.

The above synthetic approaches were successfully extended to the formation of dumbbell compounds.

Thermal and thermal oxidative stability evaluations were performed on mono- and diphospha-s-triazines at 235 and 316 °C using sealed Pyrex ampoules. The specific compounds studied were: 1-diphenylphospha-3,5-

bis(perfluoro-n-heptyl)-2,4,6-triazine, 1-diphenylphospha-3,5-bis(perfluoro-alkylether)-2,4,6-triazines, their respective pentafluorophenyl analogues, 1,3-bis(diphenylphospha)-5-perfluoro-n-heptyl-2,4,6-triazine and 1,3-bis-(diphenylphospha)-5-perfluoroalkylether-2,4,6-triazine. All the compounds wherein phenyl groups were present on the phosphorus exhibited good thermal stability up to 316°C; the analogous pentafluorophenyl substituted materials were degraded extensively at these temperatures. The oxidative stability of both the mono- and diphospha-s-triazines was excellent at 235°C, but at 316°C some degradation was observed. This was more pronounced in compounds containing the perfluoroalkyl moiety on carbon than in the perfluoroalkylether substituted members of the series.

The symmetrical diphosphatetraazacyclooctatetraenes were obtained from the interaction of perfluoroalkyletheramidines and trichlorophosphoranes. Using this procedure, a mixture of products was afforded. The unsymmetrical isomers were prepared in excellent yields, (>80%), from perfluoroalkyletherimidoylamidines and imido-tetraphenyl-diphosphinic acid trichloride. The specific representatives of the eight membered heterocycles thus far synthesized and characterized are: 1,5-bis(diphenylphospha)-3,7-bis($C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)$)-2,4,6,8-tetraazacyclooctatetraene (x = 0 and 1) and 1,3-bis(diphenylphospha)-5,7-bis($C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)$)-2,4,6,8-tetraazacyclooctatetraene (x = 0 and 1).

2. INTRODUCTION

Perfluoroalkyl- and perfluoroalkylether-substituted s-triazines have been shown to possess excellent thermal and thermal oxidative characteristics and the latter, due to their low pour points and low vapor pressures at elevated temperatures, have been identified as promising candidates for high temperature fluids applications. Selected phosphorus-containing compositions are known to increase the lubricity of fluids and some have been found to reduce corrosion of metals exposed at elevated temperatures to perfluorinated fluids.

Symmetrical triazines 3 and their triphospha analogues, the trimeric phosphazenes $^{4-7}$, have been studied extensively. A few examples of the non-fluorinated diphospha-s-triazines have recently been reported 8. Aside from the close structural similarities, s-triazines and the trimeric phosphazenes have several other features in common. These include both methods of formation as well as physical properties. For example, the fully phenylated derivatives, triphenyl-s-triazine and diphenylphosphazene trimer, can be produced by very similar types of processes, for example the trimerization of benzonitrile and the "trimerization" of diphenylphosphinous azide 10, respectively. Both compounds are known to exhibit high thermal 11 and oxidative 12 stabilities and practically identical melting points 3,13 (233 and 234°C, respectively). Interestingly, pentaphenyldiphospha-s-triazine melts in the same temperature region (239°C)⁸, which may be taken as evidence that the replacement of carbon in the s-triazine ring system by phosphorus does not alter to any significant degree the bonding characteristics of this heterocyclic ring system.

Based on the above considerations, the synthesis of a series of heterocycles containing phosphorus, carbon and nitrogen ring atoms was

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Based on the above considerations, the synthesis of a series of heterocycles containing phosphorus, carbon and nitrogen ring atoms was

undertaken with the ultimate aim of developing materials incorporating the low melting characteristics of the fluorinated triazines with the lubricating and corrosion inhibiting properties of phosphorus containing compounds.

3. RESULTS AND DISCUSSION

3.1 Monophospha-s-Triazines

Monophospha-s-triazines, which represent a novel ring system, were prepared utilizing the reaction of imidoylamidines with trichlorophosphoranes, i.e.:

The materials synthesized are listed in Table I, the actual experimental details have been given elsewhere 14 .

TABLE I
MONOPHOSPHA-s-TRIAZINES

R	R'	Yield %	MW	m.p. °C	b.p.
CF ₃ (CF ₂) ₆	C ₆ H ₅	61	989	73-74.5	380
C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)	C ₆ H ₅	73	1153	-	355
C ₃ F ₇ [OCF(CF ₃)CF ₂] ₂ OCF(CF ₃)	C ₆ H ₅	52	1485	-	385
CF ₃ (CF ₂) ₆	C ₆ F ₅	66	1169	74-75	345
C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)	C ₆ F ₅	74	1333	-	325

As can be seen from these data, regardless of the phosphorus substituent, the perfluoroalkylether containing materials were liquids whereas the compounds wherein the perfluoroalkyl group was present on the carbon were solids.

The monophospha-s-triazines exhibited characteristic absorption at 6.3 μ in the infrared and a mass spectral fragmentation pattern ¹⁵ typified by the ion $\begin{bmatrix} N \end{bmatrix}^+$

 $\begin{bmatrix} R_2 P & N \\ N = C \end{bmatrix}^+$

The monophospha-s-triazines were found to effectively inhibit oxidation of perfluoroalkylether fluids, $F - [CF(CF_3)CF_2O]_n - C_2F_5$ and to prevent the corrosion of M-50 ball bearing alloy by these fluids at elevated temperatures. The effectiveness of this action is shown by the data summarized in Table II.

TABLE II

DEGRADATION OF A PERFLUOROALKYLETHER FLUID IN THE PRESENCE

OF M-50 ALLOY COUPON AT 600°F IN OXYGEN DURING A 24 HR PERIOD a

Fluid	Additive	Охуд	en Consu	med	Total P	roducts
Used		Total		b c		ned d
g		mg	% b	mg/g ^C	mg	mg/g a
12.13	none	70.8	24.6	5.84	576.7	47.54
8.59	$1\%^{e} [R_{f}OR_{f}CN]_{2}[Ph_{2}PN]$	1.0	0.35	0.12	6.1	0.71

a) The apparatus consisted of a sealed glass tube wherein the metal coupon was suspended in the fluid; the test was conducted in pure oxygen; at the conclusion of the test, the oxygen was measured and the products were collected and measured. b) Percent of oxygen available. c) Oxygen consumed in mg/g Krytox employed. d) Products formed in mg/g Krytox employed.

e) The percent is weight percent of additive per weight of fluid.

The monophospha-s-triazines wherein phenyl-groups were present on phosphorus exhibited excellent thermal stability at 316°C. No degradation

was observed in oxidizing atmospheres at 235°C, however at 316°C a slight extent of volatiles production was noted; the latter was more pronounced with perfluoroalkyl than with the perfluoroalkylether substituted materials ¹⁶. Replacement of the phenyl group on phosphorus by pentafluorophenyl moiety led to a drastically decreased thermal and hydrolytic stability of the monophospha-s-triazine.

3.2 <u>Diphospha-s-Triazines</u>

The diphospha-s-triazines were obtained following the procedure of Schmidpeter and Ebeling $^{8}.$

$$(H_{5}C_{6})_{2}P \searrow_{N} P(C_{6}H_{5})_{2} + R_{f}C \searrow_{NH_{2}} (H_{5}C_{6})_{2}P \searrow_{N} P(C_{6}H_{5})_{2}$$

The synthetic details and materials' characteristics have been fully reported 16,18 ; the specific compounds prepared are listed in Table III.

TABLE III
DIPHOSPHA-s-TRIAZINES

R _f	Yield %	MW	m.p. C	b.p.
CF ₃ (CF ₂) ₆	32	793	84.5-85.5	
C3F7OCF(CF3)CF2OCF(CF3)	56	875	-	158/0.001 mm Hg
C ₃ F ₇ O[CF(CF ₃)CF ₂ O] ₂ CF(CF ₃)	65	1041	-	170/0.001 mm Hg

In analogy to the monophospha-s-triazines, the perfluoroalkyl substituted compounds were solids at room temperatures, whereas the perfluoroalkylether substituted materials were liquids. The diphospha-s-triazine ring system exhibited a characteristic infrared absorption at 6.55µ and afforded a specific mass spectral breakdown pattern typified by a fragment

The diphospha-s-triazines, in a manner similar to that of monophospha-s-triazines, were found to effectively inhibit oxidation of perfluoroalkylether fluids and metal corrosion as illustrated by the results given in Table IV.

TABLE IV DEGRADATION OF A PERFLUOROALKYLETHER FLUID IN THE PRESENCE OF M-50 ALLOY COUPON AT 316° C IN OXYGEN OVER A PERIOD OF 24 HR $^{\circ}$

Fluid	Additive	Оху	gen Con	sumed	Total F	roducts
Used		Total mg	% b	mg/g ^C	Form mg	ned mg/gd
12.13	none	70.8	24.6	5.84	576.7	47.54
16.36	$1\%^{e} [R_f OR_f CN] [Ph_2 PN]_2$	0.0	0.0	0.0	12.7	0.78

a) The apparatus consisted of a sealed glass tube wherein the metal coupon was suspended in the fluid; the test was conducted in pure oxygen; at the conclusion of the test, the oxygen was measured and the products were collected and measured. b) Percent of oxygen available. c) Oxygen consumed in mg/g Krytox employed. d) Products formed in mg/g Krytox employed. e) The percent is weight percent of additive per weight of Krytox fluid.

Insofar as thermal and oxidative stability is concerned, these properties were directly comparable to those of the analogously substituted monophosphastriazines.

3.3 <u>Dumbbell Mono- and Diphospha-s-Triazines</u>

To obtain materials possessing the desired properties exhibited by the monophospha- and diphospha-s-triazines and to attain at the same time increased molecular weight and thus reduced volatility in an essentially monomeric system free of end-group effects, dumbbell compounds were synthesized. The three specific compounds thus prepared are depicted below; their synthesis and properties are fully described elsewhere ^{18,19}.

Compound I, $R_f = -(CF_2)_8$

Compound II, $R_f = -CF(CF_3)[OCF_2CF(CF_3)]_mO(CF_2)_5O[CF(CF_3)CF_2O]_nCF(CF_3)$ m + n = 3

$$(C_6H_5)_2$$
 $(C_6H_5)_2$
 $(C_6H_5)_2$

Compound III

As would be expected, the triazines containing perfluoroalkylether substituents, even when the bridging group was a perfluoroalkyl moiety, were liquids at room temperature. The dumbbell diphospha-s-triazine in agreement with the results obtained for the single ring analogues was a solid, mp 168-169 °C.

3.4 <u>Eight-Membered Ring Heterocycles</u>

Inasmuch as phosphonitrilic tetramer is more stable or at least as stable as the trimer, it appeared plausible that the hetero-system composed of two PN and two CN units in the ring structure will exhibit good thermal stability

together with other desirable properties such as wide fluid range (low pour point and low vapor pressure characteristics) when substituted with suitable groups. The process depicted below yielded the symmetrical 8-membered heterocycles:

whereas employing the interaction of imidoylamidine with imido-tetraphenyldiphosphinic acid trichloride gave the unsymmetrical isomer

$$R_{2}^{C1} = R_{2}^{C1} + R_{f}^{C} = NH - N = C(NH_{2})R_{f}$$

$$R_{2}^{P} = N - PR_{2}$$

$$N \qquad N$$

$$R_{f}^{C} - N = CR_{f}$$

The four compounds prepared are listed in Table V.

TABLE V

TETRAAZACYCLOOCTATETRAENES

[(C₆H₅)₂PN]₂[R_fCN]₂

R _f	Туре	Yield	MW	spec. abs. µ	oC mp	bp °C at 0.001 mm
C ₃ F ₇ OCF(CF ₃)	sym.	32	1020	6.05	77.5-79.5	138-139
C ₃ F ₇ OCF(CF ₃)	unsym.	80	1020	6.35,6.45	126-127.5	<u>-</u>
C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)	sym.	27	1352	6.05	-	150-153
C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)		98	1352	6.35,6.80	-	146-148

As can be seen, the two "unsymmetrical" cyclooctatetraenes as represented by the general structure V have been obtained in pure form and much higher yield than the symmetrical isomers (structure IV). This is due probably to the mechanism of cyclization in the symmetrical cyclooctatetraenes, where, in a stepwise fashion, four molecules of reactants have to combine. This type of a process allows the production of diphospha and monophospha-s-triazines as well. Furthermore, the precursor perfluoroalkylether amidines invariably contained imidoylamidines which would give rise to the monophospha-s-triazines. The synthesis of the unsymmetrical cyclooctatetraenes involves interaction of two pure compounds which under specific conditions proceeds to completion with minimal occurrence of side reactions.

Both series of compounds exhibited characteristic infrared spectra as evident from the data given in Table V; no significant differences were observed in the mass spectral breakdown patterns. The unsymmetrical compounds were higher melting than the symmetrical analogues which would be expected from the presence of the $(C_6H_5)_2P=N-P(C_6H_5)_2$ arrangement. All these aspects have been reported 18 , 19 .

4. REFERENCES

- K. L. Paciorek, R. H. Kratzer, J. Kaufman, and R. W. Rosser,
 J. Fluorine Chem., 6, 241 (1975).
- C. E. Snyder, Synthesis of Fluorinated Alkoxy- and Alkyl-Substituted s-Triazines and Their Fluid Properties, AFML-TR-69-302, 1970.
- E. M. Smolin and L. Rapoport, s-Triazines and Derivatives,
 Interscience Publishers, Inc. 1959.
- 4. H. R. Allcock, Phosphorus-Nitrogen Compounds, Academic Press, 1972.
- J. R. Van Wazer, Phosphorus and Its Compounds, Interscience Publishers, Inc., 1958.
- C. P. Haber, The Chemical Society, Special Publication No. 15, 115 (1961).
- R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, Chem. Rev., <u>62</u>, 247 (1962).
- 8. A. Schmidpeter and J. Ebeling, Chem. Ber., <u>101</u>, 3883 (1968).
- 9. A. Pinner and F. Klein, Ber., 11, 764 (1878).
- 10. R. H. Kratzer and K. L. Paciorek, Inorg. Chem., 4, 1767 (1965).
- E. S. Blake, et al., J. Chem. Engin. Data, <u>6</u>, 87 (1961).
- 12. K. L. Paciorek and R. H. Kratzer, unpublished results.
- C. P. Haber, D. L. Herring, and E. A. Lawton, J. Amer. Chem. Soc., 80, 2116 (1958).
- R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, and T. I. Ito, J. Fluorine Chem., <u>10</u>, 231 (1977).

- K. J. L. Paciorek, J. H. Nakahara, and R. H. Kratzer, J. Fluorine Chem., <u>11</u>, 537 (1978).
- R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, T. I. Ito, and J. H. Nakahara, J. Fluorine Chem., <u>13</u>, 199 (1979).
- 17. R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, T. I. Ito, and J. H. Nakahara, J. Fluorine Chem., 13, 189 (1979).
- 18. Appendix, this report.
- K. J. L. Paciorek, T. I. Ito, and R. H. Kratzer, J. Fluorine Chem., to be published.

5. PRESENTATIONS AND PUBLICATIONS

- Preliminary results generated under this program were presented at AFML on 17 May 1976.
- Patent disclosure "Monophospha-s-triazines", AF Invention No. 12,317.
- 3. A paper "Perfluoroalkyl and Perfluoroalkylether Substituted Phosphas-triazines" has been presented at the 6th European Symposium on Fluorine Chemistry, Dortmund, Germany, 28 March - 1 April 1977.
- "Phospha-s-triazines. I. Synthesis and Properties of Mono(diarylphospha)s-triazines", J. Fluorine Chem., <u>10</u>, 231 (1977).
- Results generated under this program were presented at AFML on 10 June 1977.
- 6. "Phospha-s-triazines. II. Mass Spectra of Mono(diarylphospha)-s-triazines", J. Fluorine Chem., 11, 537 (1978).
- 7. Patent disclosure "Diphospha-s-triazines", AF Invention No. 13,252.
- Patent disclosure "Lubricant Composition", AF Invention No. 13,411.
- 9. "Phospha-s-triazines. III. Syntheses and Properties of 1,3-Bis(diaryl-phospha)-5-perfluoroaliphatic-2,4,6-triazines", J. Fluorine Chem., 13, 189 (1979).
- "Phospha-s-triazines. IV. Degradation Studies of 1-Diarylphospha-3,5-bis(perfluoroaliphatic)-2,4,6-triazines and 1,3-Bis(diarylphospha)-5-perfluoroaliphatic-2,4,6-triazines", J. Fluorine Chem., 13, 199 (1979).
- 11. A paper "Phospha-s-triazines and Related Heterocyclics" has been presented at the Fourth Winter Fluorine Conference, Daytona Beach, Florida, 28 January - 2 February 1979.

- 12. "Phospha-s-triazines. V. Synthesis of Dumbbell Compounds" to be submitted to the Journal of Fluorine Chemistry.
- 13. "Diphosphatetraazacyclooctatetraenes. I. Synthesis and Properties" to be submitted to the Journal of Fluorine Chemistry.
- 14. Patent disclosure "Dumbbell Phospha-s-triazines" in preparation.
- 15. Patent disclosure "Diphosphatetraazacyclooctatetraenes" in preparation.

APPENDIX

Experimental Details and Procedures pertaining to the work carried out from 1 March 1978 to 28 February 1979.

General

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inertatmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. The molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. Thermal analyses were conducted using a DuPont 951/990 Thermal Analyzer system. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 204, equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. For gas chromatographic analyses a stainless steel column, 10' x 1/8", 4% OV-101 on Chromosorb G was employed, either isothermally at 300°C or programmed at 8°C/min from 50-300°C. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of Sebacoamidine

To liquid ammonia (15 ml) at -40°C was added sebaconitrile (5.02 g, 11.10 mmol) over a period of 20 min. The solution was then stirred at -28°C for 1 hr. After warming to room temperature and ammonia removal pure sebacoamidine (5.37 g, 99.4% yield), mp 175-178°C, was obtained. This material was insoluble in refluxing common solvents including Freon-113. The mass spectrum, given in Table I, and infrared spectrum are consistent with the structural arrangement.

TABLE I

MASS SPECTRUM OF SEBACOAMIDINE a

m/e		m/e		m/e	
42	8.4	94	15.1	244	11.6
43	100	100	5.5	344	19.1
44	8.6	131	6.8	420	12.8
69	9.0	144	6.8	444	57.3
78	4.2	194	4.2	445	11.1
				486	3.5

a) Peaks below m/e 42 and having intensities less than 3% of the base peak are not reported.

Preparation of Perfluoroalkyl, Perfluoroalkylether imidoylamidine,

C₃F₇OCF(CF₃)CF₂OCF(CF₃)C(NH₂)=N-C(=NH).(CF₂)₈C(=NH)-N=C(NH₂)
CF(CF₃)OCF₂CF(CF₃)OC₃F₇

To sebacoamidine (2.03 g, 4.18 mmol) was added the ether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, (6.13 g, 12.85 mmol) and the mixture was stirred at room temperature for 5 days; subsequently the excess of nitrile (2.34 g, 4.91 mmol, 96% reaction) was removed in vacuo. The product (5.81 g, 96.7% yield; at the end of one day the reaction extent was only 54.5%) exhibited infrared and mass spectra consistent with the assigned structure.

Preparation of "dumbbell"-monophospha-s-triazine, Compound I

A mixture of the imidoylamidine, $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)C-(NH)-N=C(NH_2)]_2(CF_2)_8$ (3.00 g, 2.08 mmol) and diphenyltrichlorophosphorane (1.40 g, 4.80 mmol) was heated under nitrogen by-pass for 259 hr at 99-107°C. Subsequently, the product was dissolved in Freon-113 and purified by filtration

through a 1.5 x 3.5 cm column of Woelm neutral alumina. The viscous liquid thus obtained (2.20 g, 59% yield) was found by GC to consist of 94% of the "dumbbell" triazine, 4% of monophospha-s-triazine, $[(C_6H_5)_2PN][C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2, \text{ and 2% of unidentified products.}$

Anal. Calcd. for $C_{52}H_{20}F_{50}N_6O_4P_2$: C, 34.61; H, 1.12; F, 52.64; N, 4.66; P, 3.43; MW, 1804.

Found: C, 34.72; H, 0.98; F, 54.35; N, 4.75; P, 3.42; MW, 1800.

Preparation of "dumbbell"-monophospha-s-triazine, Compound II

A mixture of the bis-imidoylamidine, $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)-N=C(NH_2)]_2[CF(CF_3)(OCF_2CF(CF_3))_mO(CF_2)_5O(CF(CF_3)CF_2O)_nCF(CF_3)]$, (3.96 g, 1.96 mmol) and diphenyltrichlorophosphorane (1.28 g, 4.39 mmol) was stirred and heated under nitrogen by-pass for 185.5 hr at $103-117^{\circ}C$. The product mixture was dissolved in Freon-113 and purified by filtration through a 1.5 x 3.5 cm column of Woelm neutral alumina. The solvent was removed in vacuo and the residue (2.83 g, 49.4% yield) was dried at $100-110^{\circ}C$ for 13 hr.

Anal. Calcd. for $C_{26}^{H}_{20}^{F}_{70}^{N}_{6}^{O}_{9}^{P}$: C, 31.23; H, 0.85; F, 55.77; N, 3.52; P, 2.60; MW, 2384.

Found: C, 32.06; H, 1.13; F, 54.36; N, 3.77; P, 3.04; MW, 1850.

Preparation of "dumbbell"-diphospha-s-triazine, Compound III

Under nitrogen by-pass to a stirred solution of imido-tetraphenyl-diphosphinic acid trichloride (1.66 g, 3.38 mmol) in s-tetrachloroethane (15 ml) at 98° C was added sebacodiamidine (0.82 g, 1.69 mmol) over a period of 11 min. Heating at $94-101^{\circ}$ C was continued over a period of 185 hr. The residue obtained on removal of the solvent was tritiated with Freon-113 and the Freon-113 soluble portion was then treated with hot <u>n</u>-heptane. The insoluble material was redissolved in Freon-113 and filtered through a

1.5 x 3.5 cm column of Woelm neutral alumina. The material thus obtained was crystallized from a Freon-113-acetone-pentane solvent mixture to give a white powder, mp $168-169^{\circ}$ C.

Anal. Calcd. for $C_{58}^{H}_{40}^{F}_{16}^{N}_{6}^{P}_{4}$: C, 55.78; H, 3.23; F, 24.34; N, 6.73; P, 9.93.

Found: C, 55.79; H, 3.57; F, 23.10; N, 6.61; P, 10.36.

Due to the material's insolubility in common organic solvents, including hexafluorobenzene, the molecular weight could not be determined.

Interaction of C₃F₇OCF(CF₃)CF₂OCF(CF₃)C(=NH)NH₂ and Diphenyltrichlorophosphorane

a) In the absence of solvent. A mixture of the perfluoroalkylether-substituted amidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)NH_2$, (5.01 g, 10.14 mmol) and diphenyltrichlorophosphorane (3.05 g, 10.44 mmol) was heated under nitrogen by-pass for 24 hr at $108-114^{\circ}C$, then at $123-132^{\circ}C$ for an additional 144 hr. The product (6.77 g, 98.7% yield) thus obtained exhibited in its infrared spectrum strong bands at 6.0, 6.3, and 6.55 μ . Gas chromatography (isothermally at $300^{\circ}C$) showed the presence of 3 main peaks. The first peak (33%) was due to monophospha-s-triazine, $[(C_6H_5)_2PN][C_3F_7OCF(CF_3)-CF_2OCF(CF_3)CN]_2$, the next peaks (39%) were attributed to diphenylphosphate-traazacyclooctatetraenes, $[(C_6H_5)_2PN]_2[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$, and the last peak (17%) to diphospha-s-triazine, $[(C_6H_5)_2PN]_2[C_3F_7OCF(CF_3)-CF_2OCF(CF_3)CN]_2$.

The product mixture was distilled at 0.001 mm Hg; three fractions: bp $128-140^{\circ}$ C (0.23 g), bp $140-135^{\circ}$ C (2.56 g), and bp $135-136^{\circ}$ C (2.22 g) were collected. All three exhibited essentially identical infrared spectra and GC traces.

Assuming all three heterocycles to have an identical GC-response per unit weight: Calcd. Average MW, 1160; Found, 1110.

b) In s-tetrachloroethane. A mixture of the perfluoroalkylether-substituted amidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)NH_2$, (2.89 g, 5.85 mmol) and diphenyltrichlorophosphorane (1.99 g, 6.83 mmol) was heated with stirring in s-tetrachloroethane (10 ml) under a nitrogen by-pass for 163 hr at $103-105^{\circ}C$. After cooling and solvent removal in vacuo, followed by dissolution in Freon-113, filtration, and Freon evaporation, 4.09 g of product was obtained. A portion (1.3 g) of this material in Freon-113 (80 ml) was passed through a 1.5 x 3.5 cm column of Woelm neutral alumina. The product (1.13 g) was found by GC to consist of: monophospha-s-triazine, $[(C_6H_5)_2PN][C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$, (48%); tetraazacyclooctatetraene, $[(C_6H_5)_2PN]_2[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$, (45%); and diphospha-s-triazine, (8%).

Assuming all three heterocycles to have an identical GC-response per unit weight: Calcd. Average MW, 1220; Found, 1240.

c) In benzene-Freen-113 using triethylamine as an acid acceptor.

Under nitrogen by-pass, a solution of 88% amidine, $C_3F_7OCF(CF_3)CF_2OCF-(CF_3)C(=NH)NH_2$ and imidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)N=C(NH_2)-CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, (3.14 g, 6.69 mmol) and triethylamine (5.4 ml, 38.72 mmol) in Freon-113 (25 ml) was added dropwise over 28 min. to a solution of diphenyltrichlorophosphorane (3.86 g, 13.24 mmol) in benzene (25 ml) at 50°C. The resulting mixture was stirred and heated at 50°C for 113.5 hr. After cooling, Freon-113 (75 ml) was added and the insoluble portion was removed by filtration. The concentrated filtrate was then refiltered through a 1.5 x 5 cm column of Woelm neutral alumina giving a viscous liquid (3.22 g, 75% yield). Distillation failed to afford separation of monophospha- and diphospha-s-triazines from the desired cyclooctatetraene. The best fraction (0.98 g) bp 150-153°C/0.001 mm Hg contained, based on gas chromatography, 66% of cyclooctatetraene, 19% of monophospha-s-triazine, 13% of diphospha-s-triazine, and 2% of unidentified products.

Anal. Calcd. for $C_{42}^{H}_{20}^{F}_{34}^{N}_{4}^{O}_{4}^{P}_{2}$: C, 37.30; H, 1.49; F, 47.76; N, 4.14; P, 4.58; O, 4.73; MW, 1352.55.

Found: C, 38.04; H, 1.55; F, 47.77; N, 4.04; P, 4.52; MW, 1200.

Assuming all three heterocycles to have an identical GC-response per unit weight: Calcd. Average MW, 1230. The mass spectrum of the pure 1,5-bis(diphenylphospha)-3,7-bis(perfluoroalkylether)-2,4,6,8-tetraaza-cyclooctatetraene is given in Table II.

TABLE II
ION FRAGMENTS AND INTENSITIES
RELATIVE TO BASE PEAK OF

$$(C_6H_5)_2P = N - CCF(CF_3)OCF_2CF(CF_3)OC_3F_7$$

 N
 N
 $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C - N = P(C_6H_5)_2$

m/e		m/e		m/e	
69	19.8	185	4.6	551	4.2
73	3.4	199	3.4	676	7.1
77	8.0	201	19.2	693	10.0
97	3.4	202	4.8	694	16.3
100	3.7	225	30.5	695	3.5
119	12.9	226	10.5	901	100.0
147	3.5	243	18.8	902	43.9
165	3.1	244	3.5	903	14.5
169	15.9	275	3.0	1001	8.7
183	6.1	424	20.7	1002	4.0
		425	7.3	1352	2.4

a) Peaks lower than m/e 69 and those having intensities less than 3% of the base peak are not reported.

Interaction of Imido-tetraphenyl-diphosphinic Acid Trichloride and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(NH_2)=N-C(=NH)CF(CF_3)OCF_2CF-(CF_3)OC_3F_7$

a) In the absence of solvent. A mixture of perfluoroalkylethersubstituted imidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(NH_2)=N-C(=NH)-CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, (3.36 g, 3.46 mmol) and imido-tetraphenyldiphosphinic acid trichloride (1.80 g, 3.67 mmol) was heated under nitrogen by-pass for 232 hr at $102-112^{\circ}C$ and for an additional 21 hr at $137-138^{\circ}C$. The material was subsequently distilled in vacuo giving 2.30 g of fluid bp $136-142^{\circ}C$ at 0.001 mm Hg; in addition in a liquid nitrogen cooled trap 1.08 g, (32.8%) of the corresponding perfluoroalkylether nitrile, $C_3F_7OCF-(CF_3)CF_2OCF(CF_3)CN$, was collected. The distillate was shown by gas chromatography to consist of: monophospha-s-triazine, $[(C_6H_5)_2PN]-[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$, (4%); cyclooctatetraene, $[(C_6H_5)_2PN]_2-[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$, (4%); and diphospha-s-triazine, $[(C_6H_5)_2PN]_2-[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$, (4%); and diphospha-s-triazine, $[(C_6H_5)_2PN]_2-[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$, (4%); and diphospha-s-triazine,

Assuming all three heterocycles to have an identical GC-response per unit weight: Calcd. Average MW, 905; Found, 930.

b) In s-tetrachloroethane. A mixture of the perfluoroalkylether-substituted imidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(NH_2)=N-C-(=NH)-CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, (3.85 g, 3.96 mmol) and imido-tetraphenyl-diphosphinic acid trichloride (2.25 g, 4.58 mmol) was heated with stirring in s-tetrachloroethane (20 ml) under nitrogen by-pass for 144 hr at 105-111 $^{\circ}$ C. The residue obtained after removal of s-tetrachloroethane exhibited an infrared spectrum identical with that of diphospha-s-triazine, $[(C_6H_5)_2PN]_2-[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]$; the GC analysis showed only the presence of monophospha-s-triazine (5%) and diphospha-s-triazine (95%).

c) In acetonitrile-Freon-113 using triethylamine as an acid acceptor.

Under nitrogen by-pass to a solution of imido-tetraphenyl-diphosphinic acid trichloride (1.17 g, 2.38 mmol) in acetonitrile (10 ml) at 50° C was added dropwise over 1.75 hr a solution of the imidoylamidine, C_3F_7 OCF(CF_3)CF₂OCF-(CF_3)C(=NH)-N=C(NH₂)CF(CF_3)OCF₂CF(CF_3)OC₃F₇, (2.05 g, 2.11 mmol) and triethylamine (0.98 ml, 7.03 mmol) in Freon-113 (18 ml). The resulting mixture was heated at $\sim 50^{\circ}$ C for 142 hr. After solvent removal, the residue was tritiated with Freon-113 (4 x 10 ml) and then filtered through a 1.5 x 5 cm column of Woelm neutral alumina. The product thus obtained (2.80 g, 98% yield) was distilled in vacuo, bp $146-148^{\circ}$ C/0.001 mm Hg.

Anal. Calcd. for $C_{42}^{H}_{20}^{F}_{34}^{N}_{4}^{O}_{4}^{P}_{2}$: C, 37.30; H, 1.49; F, 47.76; N, 4.14; P, 4.58; O, 4.73; MW, 1352.55.

Found: C, 38.29; H, 1.55; F, 48.82; N, 4.23; P, 3.94; MW, 1400.

The mass spectrum of the pure 1,3-bis(diphenylphospha)-5,7-bis(perfluoro-alkylether)-2,4,6,8-tetraazacyclooctatetraene is given in Table III.

TABLE III
ION FRAGMENTS AND INTENSITIES
RELATIVE TO BASE PEAK OF

$$(C_6H_5)_2P = N - P(C_6H_5)_2$$

 $N N$
 $N N$
 $C_3F_7OCF(CF_3)CF_2O(CF_3)CFC - N = CCF(CF_3)OCF_2CF(CF_3)OC_3F_7$

m/e		m/e		m/e	
69	47.5	160	4.2	424	47.6
77	5.6	169	31.3	425	16.6
78	4.3	183	8.0	426	3.2
96	3.5	185	3.7	551	3.3
97	6.6	192	12.3	879	4.3
100	8.4	199	9.3	901	100.0
119	27.9	202	4.3	902	52.8
122	3.4	211	8.4	903	11.7
147	3.9	212	6.2	1001	11.8
150	3.0	225	7.3	1002	5.9
152	3.2	306	8.1	1352	5.6

a) Peaks lower than m/e 69 and those having intensities less than 3% of the base peak are not reported.

<u>Preparation of 1,5-bis(diphenylphospha)-3,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene, $[(C_6H_5)_2PN]_2[C_3F_7OCF(CF_3)CN]_2$ </u>

Under nitrogen by-pass, a solution of amidine, $C_3F_7OCF(CF_3)C(=NH)NH_2$, (2.89 g, 8.81 mmol) and triethylamine (3.9 ml, 27.96 mmol) in Freon-113 (20 ml) was added over a period of 1.7 hr to a solution of diphenyltrichlorophosphorane (5.48 g, 18.8 mmol) in benzene (50 ml) at $50^{\circ}C$. The mixture was then stirred and heated at $50^{\circ}C$ for 87 hr. After removal of solvents under reduced pressure, the residue was treated with Freon-113 (5 x 15 ml) and filtered through a 1.5 x 5 cm

column of Woelm neutral alumina. The product (2.17 g, 47% yield) was distilled in vacuo giving the desired cyclooctatetraene (1.46 g, 31.5%); bp $138-139^{\circ}\text{C}/0.001 \text{ mm Hg}$; mp $77.5-79^{\circ}\text{C}$.

Anal. Calcd. for $C_{36}^{H}_{20}^{F}_{22}^{N}_{4}^{O}_{2}^{P}_{2}^{:}$ C, 42.37; H, 1.98; F, 40.96; N, 5.49; P, 6.07; O, 3.14; MW, 1020.49.

Found: C, 42.56; H, 2.03; F, 41.14; N, 5.53; P, 5.42; MW, 1130.

The mass spectrum of the pure cyclooctatetraene is given in Table IV.

TABLE IV
ION FRAGMENTS AND INTENSITIES
RELATIVE TO BASE PEAK OF

m/e		m/e		m/e	
69	22.9	165	3.4	425	15.1
77	11.3	183	13.6	510	11.8
78	3.7	185	8.3	735	100.0
100	3.2	225	39.9	736	45.8
107	3.0	226	3.3	737	11.4
108	4.6	275	4.1	835	6.8
119	10.9	306	6.8	1001	6.1
122	3.6	424	40.0	1020	5.0

a) Peaks lower than m/e 69 and those having intensities less than 3% of the base peak are not reported.

<u>Preparation of 1,3-bis(diphenylphospha)-5,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene, [(C₆H₅)₂PN]₂[C₃F₇OCF(CF₃)CN]₂</u>

Under nitrogen by-pass to a solution of imido-tetraphenyldiphosphinic acid trichloride (1.79 g, 3.65 mmol) in acetonitrile (22 ml) at 50° C was added a solution of imidoylamidine, C_3F_7 OCF(CF₃)C(=NH)N=C(NH₂)CF(CF₃)OC₃F₇, (2.0 g, 3.13 mmol) and triethylamine (1.38 ml, 9.89 mmol) in Freon-113 (7 ml). The mixture was then stirred at 50° C for 111.3 hr. Following solvent removal, the Freon-113 soluble material (3.19 g, 80% yield) was crystallized from Freon-113/acetone/pentane; mp 126-127.5°C.

Anal. Calcd. for $C_{36}^{H}_{20}^{F}_{22}^{N}_{4}^{O}_{2}^{P}_{2}$: C, 42.37; H, 1.98; F, 40.96; N, 5.49; P, 6.07; O, 3.14; MW, 1020.49.

Found: C, 42.64; H, 2.09; F, 41.33; N, 5.45; P, 6.07; MW, 1050.

The mass spectrum of the cyclooctatetraene is given in Table V.

TABLE V
ION FRAGMENTS AND INTENSITIES
RELATIVE TO BASE PEAK OF

$$(C_6H_5)_{2_1}^{P=N-P(C_6H_5)_2}$$

 N_{II}
 $C_3F_7O(CF_3)CFC-N=CCF(CF_3)OC_3F_7$

m/e		m/e		m/e		
69	24.0	191	3.3	425	31.1	
77	6.3	192	10.3	426	4.1	
78	4.4	198	3.0	551	3.7	
100	3.7	199	11.3	735	100.0	
108	3.0	200	5.6	736	53.1	
119	9.0	202	3.1	737	12.9	
122	6.1	212	14.7	835	7.8	
153	3.7	225	3.8	836	3.9	
160	4.4	272	3.3	1001	6.2	
183	15.0	306	12.1	1019	3.4	
184	3.7	307	3.2	1020	21.9	
185	5.6	424	75.0	1021	8.0	

a) Peaks lower than m/e 69 and those having intensities less than 3% of the base peak are not reported.